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(54) Title: MEDICAL, DENTAL AND ORTHODONTIC ARTICLES OF Ni-Ti-Nb ALLOYS

(57) Abstract

Dental and orthodontic articles are made of Ni-Ti-Nb alloys possessing both superelastic and shape memory properties. The articles may be orthodontic archwires, tubes, springs or the like, or other medical/dental articles. The alloy desirably has a minimum loading force of at least 800 MPa and a minimum unloading force of at least 400 MPa, while exhibiting superelastic deformation in the range of 8 %-14 % prior to exhibiting plastic deformation when subjected to a load.

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MEDICAL, DENTAL AND ORTHODONTIC ARTICLES OF Ni-Ti-Nb ALLOYS

Related Applications

This application is a continuation-in-part application of Serial No. 08/221,638, filed March 31, 1994.

Field of the Invention

The invention relates to medical, dental and orthodontic articles, and more particularly to such articles made from Ni-Ti-Nb alloys having shape memory and super-elastic characteristics.

Background to the Invention

Ni-Ti based alloys are known to exhibit shape memory properties associated with transformations between martensite and austenite phases. These properties include thermally induced changes in configuration in which an article is first deformed from a heat-stable configuration to a heat-unstable configuration. Subsequent exposure to increased temperature results in a change in configuration from the heat-unstable configuration towards the original heat-stable configuration.

These alloys also exhibit enhanced elastic properties compared with materials which do not exhibit martensite-austenite

transformations. The superelastic transformation of shape memory alloys is discussed in "Engineering Aspects of Shape Memory Alloys", T. W. Duerig et al., p. 370, Butterworth-Heinemann (1990), the subject matter of which is hereby incorporated in this specification by this reference. The transformation is depicted in Fig. 1 of the accompanying drawings. Figure 1 shows how stress varies with strain during reversible elastic deformation. It will be understood that, as strain increases, stress increases initially approximately linearly. This behavior is reversible, and corresponds to conventional elastic deformation. Subsequent increases in strain are accompanied by little or no increase in stress, over a limited range of strain to the end of the "loading plateau". The loading plateau stress is defined by the inflection point on the stress/strain graph. Subsequent increases in strain are accompanied by increases in stress. On unloading, there is a decline in stress with declining strain to the start of the "unloading plateau," as evidenced by the existence of an inflection point (which is characteristic of the superelastic behavior with which the present invention is concerned) along which stress changes little with reducing strain. At the end of the unloading plateau, stress reduces with reducing strain. The unloading plateau stress is also defined by an inflection point on the stress/strain graph. Any residual strain after unloading to zero stress is the permanent set of the sample.

Characteristics of the elastic deformation, the loading plateau, the unloading plateau, the elastic modulus, the plateau length and the permanent set (defined with respect to a specific total deformation) are established, and are defined in, for example, "Engineering Aspects of Shape

Memory Alloys", at page 376. Typical values for commercially available Ni-Ti binary alloys are:

Loading plateau stress	500 MPa
Unloading plateau stress	150-280 MPa
Permanent set (after 6% deformation)	< 0.5%
Plateau length	6%-8%
Elastic modulus	40-50 GPa

The thermally-induced recovery, shape memory properties of Ni-Ti-Nb based alloys have been investigated. It has been found that the characteristic temperatures of the shape transformation of certain Ni-Ti-Nb based alloys can be modified by appropriate treatment, so that alloys which would normally exist in the austenite phase at ambient temperature can be stored in the martensite phase at room temperature in a deformed configuration from which they will recover when heated. Such alloys are disclosed in EP-A-185452. The advantageous properties of the Ni-Ti-Nb based alloys disclosed in EP-A-185452 lie in their ability to respond to a treatment to change temporarily the characteristic temperatures of the thermally induced change in configuration. No consideration has been given to their superelastic properties. Indeed, the fact that the transformation hysteresis can be expanded in the way referred to above (i.e., to make an alloy stable temporarily at ambient temperature in the martensite phase) suggests that such alloys would not be useful as superelastic alloys. Also, it is established that preferably the transformation hysteresis is as small as possible in a superelastic alloy. See, e.g., "Engineering Aspects of Shape Memory Alloys", T. W. Duerig et al., p. 382, Butterworth-Heinemann (1990).

What is needed is a shape memory alloy that also possesses superelastic properties and which is temporarily stable in the martensite phase at room temperature in a deformed configuration, so as to be useful in a variety of medical, dental and orthodontic articles.

Summary of the Invention

The present invention is concerned with the previously unrecognized superelastic behavior of Ni-Ti-Nb alloys, having properties which are superior to those of other alloys which exhibit superelastic behavior, such as Ni-Ti binary alloys.

In broad terms, the invention provides a method of processing a Ni-Ti-Nb based alloy which comprises working an article formed from such an alloy at a temperature which is less than the recrystallization temperature of the alloy. Recrystallization of an alloy involves the formation of new, defect-free, low energy grains or crystals, which consume and replace highly worked, high energy grains. It involves the loss of a textured structure introduced by working. The invention also provides articles, particularly medical, dental and orthodontic articles, formed from such alloys.

Accordingly, in one aspect, the invention provides a method of processing a Ni-Ti-Nb based alloy which contains from about 4 to about 14 atomic percent Nb and in which the ratio of atomic percent Ni to atomic percent Ti is from about 0.8 to 1.2, comprising subjecting the alloy to at least about 10% work by a technique which comprises at least one of rolling and drawing, and operations which produce a similar textured crystal

structure in the alloy, at a temperature below the recrystallization temperature of the alloy.

The method of the invention gives rise to beneficial properties in the processed alloy. In particular, the plateau stresses of both loading and unloading are increased significantly vis-a-vis conventional binary alloys. Furthermore, the permanent set for a given deformation can in some circumstances be reduced compared with such conventional alloys. These benefits are important as they make it possible for articles to be made which can store relatively larger amounts of elastic energy per unit volume of material. As a corollary, they make it possible to keep small the size of components made using the article, yet realize greater loading and unloading forces. The increased stiffness that is apparent in articles made using the treated alloy is an attractive feature when the articles are used in, for example, medical, dental and orthodontic applications such as eyeglass frames, orthodontic archwires, tubes and springs, and guidewires for catheters. The method of the invention provides this increased stiffness without an undesirable permanent set, which has accompanied previous attempts to increase stiffness in superelastic, shape memory alloy materials, as for example by varying the compositions of the alloys.

A further advantage of the alloys of the invention is that the tendency found in some Ni-Ti based alloys to revert to an R-phase (a transitional phase between the austenite and martensite phases) is reduced. This in turn reduces the tendency of the elastic modulus to be lowered, which is important for certain applications, for example when the alloy is used in a

catheter guidewire or an orthodontic archwire where the modulus controls the geometric stability of the wire against lateral stresses.

Yet another advantage of the invention is that it provides articles with superelastic properties which are more resistant to corrosion than articles formed from alloys used previously for their superelastic properties. An advantage arising from the corrosion resistance is the biocompatibility of the materials, which makes them particularly suitable for use in medical, dental and orthodontic applications.

These and other features and advantages of the invention will be appreciated by persons skilled in the art upon review of the detailed description which follows taken in conjunction with the drawings.

Brief Description of the Drawings

Fig. 1 is a generic representation of the stress-strain relationship for a superelastic, shape-memory alloy;

Fig. 2 is the stress-strain relationship for a superelastic, shape-memory Ni-Ti-Nb alloy according to the present invention; and

Fig. 3 is the stress-strain relationship for a superelastic, shape-memory NiTi binary alloy, as known in the prior art.

Detailed Description of the Invention

The present invention provides Ni-Ti-Nb based alloys whose superelastic properties are such that: (a) the loading plateau on loading at 25°C is at least about 600 MPa, preferably at least about 700 MPa, more preferably at least about 800 MPa, and even more preferably at least about 900 MPa; and (b) the permanent set after tensile deformation of 6% at 25°C

is less than about 2.5%, preferably less than about 1.5%, and more preferably less than about 1.0%.

In the preferred method, work is imparted to the alloy by a technique which comprises at least one of rolling and drawing, and similar operations which produce a textured crystal structure. Surprisingly, it has been found that the beneficial properties which result from the method of the invention arise from working by these techniques. By working the alloy using rolling or drawing (including die-less drawing) or similar techniques, it has been found to be possible to produce an alloy which displays good ductility and good strength. Other working techniques can produce alloys with one of these properties, but not both. Particularly preferred working techniques include rod and wire drawing.

The alloys on which the method is practiced comprise nickel, titanium and niobium. It is preferred that the alloy contains at least about 4 at.% niobium, more preferably at least about 6 at.%, and even more preferably at least about 9 at.%. Furthermore, it is preferred that the alloy contains not more than about 14 at.% niobium, more preferably not more than about 12 at.%, and even more preferably not more than about 10 at.%. Additionally, it is preferred that the ratio of atomic percent Ni to atomic percent Ti is in the range of about 0.8-1.2, and more preferably in the range of about 0.9-1.1.

The alloy may contain a quantity of an element other than nickel, titanium and niobium for the purpose of regulating the transformation temperature (A_f) at which the alloy is transformed from the austenite phase to

the martensite phase, and vice versa. Examples of suitable additional elements include Fe, Co, Cr, V and Al. When such an additional element is included, it is appropriate to adjust the Ni/Ti ratio to maintain the characteristic transformation temperatures of the alloy (especially the A_s temperature) at appropriate levels.

The method of the invention may comprise subjecting the article made from the alloy to work under warm work conditions; that is, at a temperature less than the recrystallization temperature, but greater than the temperature at which recovery processes take place. Preferred conditions for such working might be, for example, at a temperature which is greater than about 300°C, more preferably greater than about 400°C, and even more preferably greater than about 450°C. The warm working will preferably be conducted at a temperature not greater than about 700°C, more preferably not greater than about 625°C, and even more preferably not greater than about 500°C.

The method of the invention alternatively may comprise subjecting the article made from the alloy to work under cold work conditions; that is, at a temperature less than that at which a significant level of recovery processes take place. Preferred conditions for such working might be, for example, at a temperature which is higher than about -100°C, more preferably higher than about -50°C, and even more preferably higher than about 10°C. The cold working will preferably be conducted at a temperature not greater than about 200°C, more preferably not greater than about 100°C, and even more preferably not greater than about 50°C. In the

case of either warm working or cold working, the alloy can be annealed before it is worked.

The method of the invention may further include a step in which the alloy is heat treated after it has been worked. When it is heat treated in this way, the work that is to be measured in the context of the method of the invention is the work that is imparted after the final drawing and prior to the final heat treatment. It is particularly preferred that the method includes a subsequent heat treatment step when the alloy is cold worked. The heat treatment is preferably carried out at a temperature which is less than the recrystallization temperature of the alloy. For example, the heat treatment may be carried out at a temperature not more than about 700°C, preferably less than about 625°C, and more preferably less than about 500°C. The heat treatment is preferably carried out at a temperature which is greater than about 300°C, and more preferably greater than about 400°C. The duration of the heat treatment step depends on the temperature that is chosen and is readily ascertainable by persons skilled in the art.

The amount of work imparted to the article should be at least 10%, more preferably at least 12%, even more preferably at least about 15%, and even more preferably at least 20%. The work can be measured as a change in cross-sectional area of the article. Preferably, the cross-sectional area of the article after the working step of the method will not exceed about 5 mm^2, more preferably it will not exceed about 3.5 mm^2, and even more preferably it will not exceed about 2.5 mm^2.

The method of the invention may include steps in addition to the working and optional heat treatment steps described above. Such additional steps include, for example, bending, swaging, pressing and so on. Any such additional steps should generally be carried out after the working and heat treatment steps.

The articles of the invention are comprised of an alloy of Ni, Ti and Nb processed according to the above-described methodology, so as to possess both shape-memory and superelastic properties, and may be configured for any one of a number of different applications. For example, the articles may be in the form of wires or tubes. The articles might be used in eyeglass frames. The articles are suitable for use in medical, dental and orthodontic applications, for example as an orthodontic wire, an orthodontic coil spring, an endosseous dental implant, endodontic reamers and files and other instruments used in dentistry, a catheter, a catheter guidewire, flexible cutting tools for arthroscopic procedures or tissue excision and other instruments used in surgery (such as reamers and files), vascular clips, vascular, biliary and urological stents, bone anchor pins, and as components (such as a spring) of any of these articles. The articles may also be used in a suture needle or a surgical needle.

Particularly in the context of orthodontic treatment, and especially after the initial stage of tooth leveling and alignment, articles according to the present invention are highly advantageous. The reasons for their significant advantages are the increased stiffness and forces provided by the shape-memory, superelastic Ni-Ti-Nb alloys of the invention vis-a-vis

know Ni-Ti alloys used in the field of orthodontics. Specifically, the Ni-Ti-Nb alloys treated in accordance with the method of this invention exhibit greater stiffness, combined with greater resilience, as compared to known Ni-Ti alloys used in orthodontics. For example, the loading and unloading forces exhibited by articles of the present invention are approximately double or more than the loading and unloading forces of known alloys. While these characteristics make these high-stiffness, superelastic alloys particularly suitable for orthodontic archwires, including intermediate wires, and various springs, they are also well-suited for brackets and other fixed orthodontic appliances.

In another aspect, the invention provides an article which comprises at least one component formed from a Ni-Ti-Nb based alloy processed as described herein, wherein the component exhibits superelastic and shape memory properties. The article can be used in, for example, any of the applications referenced above.

EXAMPLE 1

A Ni-Ti-Nb wire with a circular cross-section and an initial diameter of 0.54 mm, and a composition of 46 at.% Ni, 45 at.% Ti and 9% Nb, was heat treated at 600°C and drawn to a diameter of 0.45 mm (leaving 33% cold work in the material). After drawing at room temperature, the wire was heat treated at 400°C for 10 minutes. Room temperature tensile testing gave the following properties:

Loading plateau stress	900 MPa
Unloading plateau stress	500 MPa
Permanent set (after 6% deformation)	0.3%
Plateau length	8.5%

Young's modulus	65 GPa

Figure 2 shows the properties of the resulting wire described in the above Example 1 compared to the analogous properties of a typical archwire such as is commercially available from Raychem under the trade name Alloy BB, which are shown in Figure 3.

It will be appreciated that the recovery stresses which are obtainable in articles of the present invention can be modified in one of several ways: (1) varying the amount of the Nb alloying element; (2) including a fourth element, such as Fe, Co, Cr, V and Al; (3) modifying the cold work ratio; and/or (4) modifying the temperature at which the heat treatment is performed.

The invention is disclosed in this specification with reference to specific features. It will be apparent that modifications can be made to the invention as disclosed. Accordingly, the scope of the protection is to be defined by the claims.

What is claimed is:

1. A dental or orthodontic article comprising an alloy of Ni, Ti and Nb, said alloy possessing both shape memory and superelastic properties.

2. An article according to claim 1 wherein the minimum loading force of said alloy is greater than about 800 MPa.

3. An article according to claim 2 wherein said minimum loading force is about 1000 MPa.

4. An article according to claim 1 wherein the minimum unloading force of said alloy is greater than about 400 MPa.

5. An article according to claim 4 wherein said minimum unloading force is about 650 MPa.

6. An article according to claim 1 wherein said alloy exhibits superelastic deformation greater than about 8% prior to exhibiting plastic deformation when subjected to a load.

7. An article according to claim 6 wherein said superelastic deformation is in the range of about 8%-14%.

8. An article according to claim 1 in the form of an orthodontic archwire.

9. An article according to claim 1 in the form of an orthodontic tube.

10. An article according to claim 1 in the form of a spring.

11. An article according to claim 1 wherein said alloy contains from about 4 to about 14 atomic percent Nb and in which the ratio of atomic percent Ni to atomic percent Ti is from about 0.8 to 1.2.

12. An article according to claim 11 wherein said alloy includes an additional element selected from Fe, Co, Cr, V and Al.

13. A dental or orthodontic article comprising an alloy of Ni, Ti and Nb, said alloy possessing both shape memory and superelastic properties, wherein said alloy has a minimum loading force of about 800 MPa and a minimum unloading force of about 400 MPa.

14. An article according to claim 13 wherein said minimum loading force is about 1000 MPa and said minimum unloading force is about 650 MPa.

15. An article according to claim 13 wherein said alloy exhibits superelastic deformation of at least about 8% prior to exhibiting plastic deformation when subjected to a load.

16. An article according to claim 15 wherein said superelastic deformation is in the range of about 8%-14%.

17. An article according to claim 13 in the form of an orthodontic archwire, tube or spring.

18. An article according to claim 13 wherein said alloy contains from about 4 to about 14 atomic percent Nb and in which the atomic percent Ni to atomic percent Ti is from about 0.8 to 1.2.

19. An article according to claim 18 wherein said alloy includes an additional element selected from Fe, Co, Cr, V and Al.

AMENDED CLAIMS

[received by the International Bureau on 18 October 1996 (18.10.96);
original claims 11 and 18 cancelled;
original claims 1, 12 and 13 amended;
remaining claims unchanged (3 pages)].

1. A dental or orthodontic article comprising an alloy of Ni, Ti, and Nb, said alloy possessing both shape memory and superelastic properties, and said alloy containing from about 4 to about 14 atomic percent Nb and in which the ratio of atomic percent Ni atomic percent Ti is from about 0.8 to 1.2.

2. An article according to claim 1 wherein the minimum loading force of said alloy is greater than about 800 MPa.

3. An article according to claim 2 wherein said minimum loading force is about 1000 MPa.

4. An article according to claim 1 wherein the minimum unloading force of said alloy is greater than about 400 MPa.

5. An article according to claim 4 wherein said minimum unloading force is about 650 MPa.

6. An article according to claim 1 wherein said alloy exhibits superelastic deformation greater than about 8% prior to exhibiting plastic deformation when subjected to a load.

7. An article according to claim 6 wherein said superelastic deformation is in the range of about 8%-14%.

8. An article according to claim 1 in the form of an orthodontic archwire.

9. An article according to claim 1 in the form of an orthodontic tube.

10. An article according to claim 1 in the form of a spring.

12. An article according to claim 1 wherein said alloy includes an additional element selected from Fe, Co, Cr, V and Al.

13. A dental or orthodontic article comprising an alloy of Ni, Ti, and Nb, said alloy possessing both shape memory and superelastic properties, said alloy containing from about 4 to about 14 atomic percent Nb and in which the atomic percent Ni to atomic percent Ti is from about 0.8 to 1.2, wherein said alloy has a minimum loading force of about 800 MPa and a minimum unloading force of about 400 MPa.

14. An article according to claim 13 wherein said minimum loading force is about 1000 MPa and said minimum unloading force is about 650 MPa.

AMENDED SHEET (ARTICLE 19)

15. An article according to claim 13 wherein said alloy exhibits superelastic deformation of at least about 8% prior to exhibiting plastic deformation when subjected to a load.

16. An article according to claim 15 wherein said superelastic deformation is in the range of about 8%-14%.

17. An article according to claim 13 in the form of an orthodontic archwire, tube or spring.

19. An article according to claim 18 wherein said alloy includes an additional element selected from Fe, Co, Cr, V and Al.

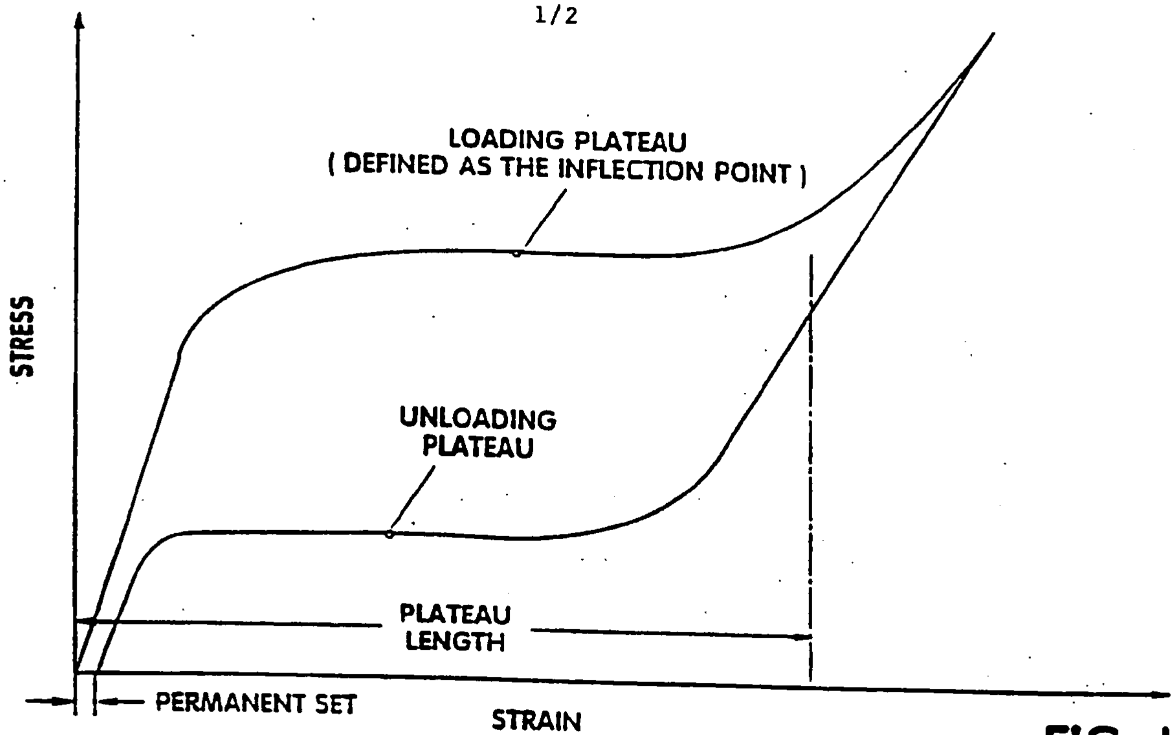
LOADING PLATEAU
(DEFINED AS THE INFLECTION POINT)
STRESS
UNLOADING
PLATEAU
PLATEAU
LENGTH
PERMANENT SET
STRAIN

FIG. 1

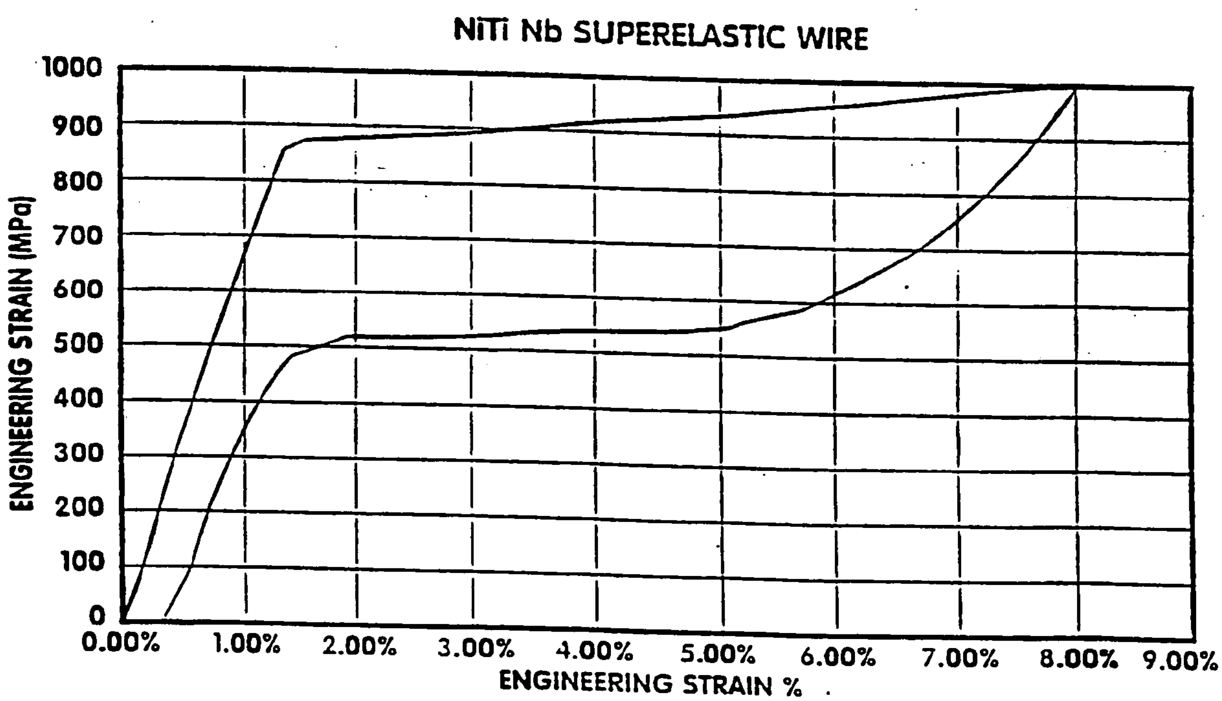
NiTi Nb SUPERELASTIC WIRE
ENGINEERING STRAIN (MPa)
1000
900
800
700
600
500
400
300
200
100
0
0.00%
1.00%
2.00%
3.00%
4.00%
5.00%
6.00%
7.00%
8.00%
9.00%
ENGINEERING STRAIN %

FIG. 2

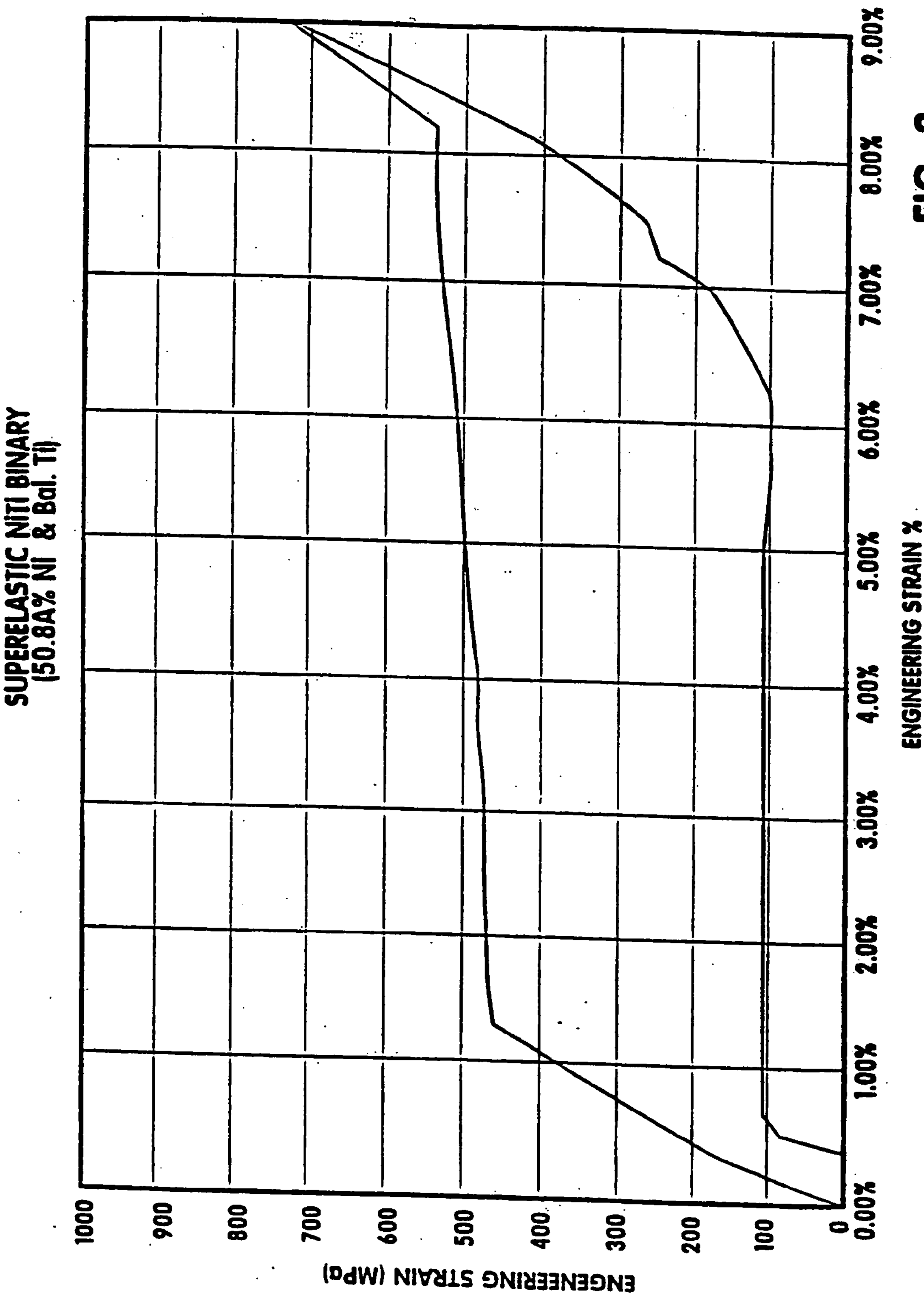
SUPERELASTIC NiTi BINARY
(50.8A% Ni & Bal. Ti)
ENGENEERING STRAIN (MPa)
1000
900
800
700
600
500
400
300
200
100
0
0.00%
1.00%
2.00%
3.00%
4.00%
5.00%
6.00%
7.00%
8.00%
9.00%
ENGINEERING STRAIN %

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/08015

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C22C 14/00, 30/00, 16/00, 27/00
US CL : 148/421, '02, 407, 442; 420/417, 580
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/421, 402, 407, 442; 420/417, 580

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,358,796 (NAKAMURA ET AL.) 25 OCTOBER 1994 (25.10.94), see column 1, lines 35 to 39.	8-10 and 17
X ---- Y	US, A, 4,770,725 (SIMPSON ET AL.) 13 September 1988 (13.09.88), see column 6, Table 2, Alloy B and column 8, Table 5, Alloys 5, 6, 8, 9, 11, and 13-15.	1-7, 11-16, 18 and 19 ---------- 8-10 and 17
X ---- Y	US, A, 4,631,094 (SIMPSON ET AL.) 23 December 1986 (23.12.86), see column 3, Example 3.	1-7, 11-16, 18 and 19 ---------- 8-10 and 17
X ---- Y	JP, A, 58-157934 (HITACHI KINZOKU KK) 20 September 1983 (20.09.83), page 188, all the examples in the table.	1-7, 11-16, 18 and 19 ---------- 8-10 and 17

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 AUGUST 1996	27 AUG 1996

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	John P. Sheehan
Facsimile No. (703) 305-3230	Telephone No. (703) 308-3861

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	JP, A, 63-096234 (TOHOKU METAL IND. LTD.) 27 April 1988 (27.04.88), page 85, the table, Examples 2, 5 and 14.	1-7, 11-16, 18 and 19 ----------- 8-10 and 17